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(54) **PROCEDE DE PHOSPHATATION DE FEUILLARD D'ACIER GALVANISE D'UN SEUL COTE**  
(54) **PHOSPHATIZATION OF A SINGLE-FACE GALVANIZED STEEL STRIP**

(57)

The invention relates to the phosphatization of the galvanized side of a single-face galvanized steel strip using a phosphatizing solution containing 1- 6 g/l zinc ions and 10-30 g/l phosphate ions. The invention is characterized in that the phosphatizing solution contains one or several constituents a) to c): a) 60-1000 mg/l of one or several monovalent or multivalent alcohols with at least a triple bond between two carbon atoms, b) 10-160 mg/l of one or several alkyl or alkenyl nitrogen compounds with at least 5 C atoms and c) 10- 250 mg/l alkali metal iodide. Preferably, the phosphatizing solution contains at least 2 and especially all 3 constituents a), b) and c).



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(54) **PROCEDE DE PHOSPHATATION DE FEUILLARD D'ACIER  
GALVANISE D'UN SEUL COTE**  
(54) **PHOSPHATIZATION OF A SINGLE-FACE GALVANIZED  
STEEL STRIP**

(57) L'invention concerne un procédé de phosphatation de feuillard d'acier galvanisé d'un seul côté, au moyen d'une solution de phosphatation qui contient 1 à 6 g/l d'ions zinc et 10 à 30 g/l d'ions phosphate. L'invention est caractérisée en ce que la solution de phosphatation contient en outre un ou plusieurs des composants suivants: a) 60 à 1000 mg/l d'un ou plusieurs alcools monovalents ou polyvalents comportant au moins une liaison triple entre deux atomes de carbone, b) 10 à 160 mg/l d'un ou plusieurs composés d'alkyle-azote ou d'alcényle-azote comportant au moins 5 atomes de carbone et c) 10 à 250 mg/l d'iodure de métaux alcalins. De préférence, la solution de phosphatation contient au moins deux des composants a), b) et c), et en particulier les trois.

(57) The invention relates to the phosphatization of the galvanized side of a single-face galvanized steel strip using a phosphatizing solution containing 1-6 g/l zinc ions and 10-30 g/l phosphate ions. The invention is characterized in that the phosphatizing solution contains one or several constituents a) to c): a) 60-1000 mg/l of one or several monovalent or multivalent alcohols with at least a triple bond between two carbon atoms, b) 10-160 mg/l of one or several alkyl or alkenyl nitrogen compounds with at least 5 C atoms and c) 10-250 mg/l alkali metal iodide. Preferably, the phosphatizing solution contains at least 2 and especially all 3 constituents a), b) and c).



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Abstract**Phosphatising steel strip which has been galvanised on one face**

A process for phosphatising the galvanised face of steel strip which has been galvanised on one face using a phosphatising solution which contains 1 to 6 g/l of zinc ions and 10 to 30 g/l of phosphate ions, characterised in that the phosphatising solution also contains one or more of the components (a) to (c): (a) 60 to 1000 mg/l of one or more mono- or poly-hydric alcohols having at least one carbon-carbon triple bond, (b) 10 to 160 mg/l of one or more alkyl or alkenyl nitrogen compounds having at least 5 carbon atoms, and (c) 10 to 250 mg/l of an alkali metal iodide. The phosphatising solution preferably contains at least two and in particular all three of components (a), (b) and (c).

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**Phosphatising steel strip which has been galvanised on one face**

This invention relates to a process for phosphatising the galvanised face of steel strip which has been galvanised on one face, the non-galvanised face not being phosphatised. Selective phosphatising of the galvanised face is achieved by adding to the phosphatising solution components which are appropriate for inhibiting phosphatising of the non-galvanised steel face but which do not impair phosphatising of the galvanised face. The use of physical methods to cover the steel face during the required phosphatising of only the galvanised face are, therefore, unnecessary.

- 10 In the context of the present invention, all references to steel strip which has been galvanised on one face are to be understood to be to electrolytically galvanised or alloy galvanised steel strip. If the latter, then the zinc layer also contains alloying constituents, such as iron, nickel and/or aluminum.
- 15 Processes for phosphatising surfaces of iron, steel, zinc and alloys thereof and of aluminum and alloys thereof have long been known in the prior art. Phosphatising of the surfaces mentioned is used to increase the strength of adhesion of lacquers and to improve the corrosion protective properties. Phosphatising is performed by immersion of the metal surfaces in phosphatising solutions or by spraying the metal surfaces with phosphatising solutions. Combined processes have also been disclosed.
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Either shaped metal parts, such as car bodies, or metal strips in high-speed conveyer belt systems may be phosphatised. The present invention is concerned with strip phosphatising of the latter type. Strip phosphatising differs from part phosphatising in that, due to the high conveyer belt speeds, the phosphatising process, i.e. the deposition of a sealed metal phosphate layer, has to take place within a short time-span of, for example, about 2 to about 20 seconds.

Processes for phosphatising metal strips, in particular electrolytically or hot dip galvanised steel strips have been disclosed in the prior art. For example, WO 91/02829 describes a process for phosphatising electrolytically and/or hot dip galvanised steel strip by short-term

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treatment using acid phosphatising solutions which contain, in addition to zinc and phosphate ions, manganese and nickel cations and anions of oxygen-containing acids having an accelerator effect. The last-mentioned component is understood to be, in particular, nitrate ions. DE-A-35 37 108 also describes a process for phosphatising electrolytically galvanised steel strips by treatment using acid phosphatising solutions which contain, in addition to zinc, manganese and phosphate ions, other metal cations, such as nickel ions and/or anions of oxygen-containing acids having an accelerator effect, in particular nitrate ions. The concentration of zinc cations is then within the relatively low range of 0.1 to 0.8 g/l.

- 10 DE-A-197 40 953 describes a process for phosphatising steel strip, or steel strip which has been galvanised or alloy galvanised on one face or on both faces, by spraying with or immersing in, for a period in the range from 2 to 20 seconds, an acid phosphatising solution which contains zinc, magnesium and manganese at a temperature in the range 50 to 70°C, characterised in that the phosphatising solution contains no nitrate ions and that it contains:
- 15 1 to 4 g/l of zinc ions,  
1.2 to 4 g/l of manganese ions,  
1 to 4 g/l of magnesium ions,  
10 to 30 g/l of phosphate ions,  
0.1 to 3 g/l of hydroxylamine in the free, ionic or bound form,
- 20 with a concentration of free acid in the range from 0.4 to 4 points and a concentration of total acid in the range from 15 to 45 points.

If nickel ions are also added to zinc- and manganese-containing phosphatising solutions, then so-called "trication" phosphatising solutions are obtained.

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When phosphatising steel strip which has been galvanised on one face, it is generally desired that only the galvanised face be phosphatised, while the non-galvanised face is intended to remain uncoated. The steps taken to achieve this objective, however, should not passivate the non-galvanised face so completely that, after shaping and joining together components from the steel strip and cleansing the assembled part, subsequent part phosphatising is prevented.

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The prior art discloses, for example, adding organic acids (acetic or tartaric acid) or amines (urea) to the phosphatising solution for this purpose. However, such use of an additive is associated with the disadvantage that the weight per unit area of the phosphatising layer on the zinc face, in particular during prolonged production, drops below the required value.

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Furthermore, it is known that the phosphatising solution should have a comparatively low pH, and thus a comparatively high free acid value, in order to avoid phosphatising the steel face of steel strip which has been galvanised on one face. However, this type of phosphatising solution exerts a high pickling effect on the zinc face, so the phosphatising solution becomes greatly enriched with zinc ions. There is then the risk that the zinc concentration reaches the solubility limit for zinc phosphate and zinc phosphate is deposited on the steel face.

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This disadvantage has resulted in large producers of phosphatised steel strip which is galvanised on one face changing over to physical methods for preventing the non-galvanised steel face coming into contact at all with the phosphatising solution. The mechanical covering procedures required for this are complicated and make the production unit much more costly.

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Attempts to inhibit phosphatising of the non-galvanised steel face by adding pickling inhibitors have hitherto been unsuccessful. These types of additives have hitherto led to the phosphatising reaction on the galvanised face, which is very sensitive to changes in operating parameters, taking place either unsatisfactorily or not at all.

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Therefore, there is a need for a process for phosphatising only the galvanised face of steel strip which has been galvanised on one face, which does not require mechanical covering procedures, but which, nevertheless, does not have the disadvantages mentioned above.

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The present invention relates to a process for phosphatising steel strip which has been galvanised on one face using a phosphatising solution which contains 1 to 6 g/l of zinc ions and 10 to 30 g/l of phosphate ions, characterised in that the phosphatising solution also contains one or more of the components (a) to (c):

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(a) 60 to 1000 mg/l of one or more mono- or poly-hydric alcohols having at least one

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carbon-carbon triple bond,

- (b) 10 to 160 mg/l of one or more alkyl or alkenyl nitrogen compounds having at least 5 carbon atoms,
- (c) 10 to 250 mg/l of an alkali metal iodide.

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In a preferred embodiment, the process is characterised in that the phosphatising solution contains one or more of components (a) to (c) in the following concentrations:

- (a) 200 to 400 mg/l of one or more mono- or poly-hydric alcohols having at least one carbon-carbon triple bond,
- 10 (b) 30 to 60 mg/l of one or more alkyl or alkenyl nitrogen compounds having at least 5 carbon atoms,
- (c) 40 to 100 mg/l of an alkali metal iodide.

15 The individual components (a), (b) and (c) hinder or inhibit the pickling reaction of the phosphatising solution with the non-galvanised steel surface so that this is not phosphatised, or is phosphatised only very slightly. The pickling reaction at the galvanised surface, however, is not hindered so that the desired, scaled, crystalline, zinc phosphate layer is built up to the desired weight per unit area on this face.

20 The expression weight per unit area is frequently used in the field of phosphatising metal surfaces. The expressions "weight deposited per unit area" or "area-specific weight" are also used instead of "weight per unit area", or more specifically "weight of phosphate layer per unit area". These expressions are to be understood to mean the weight of metal phosphate layer produced on the metal surface by the phosphatising process with reference to one unit of

25 area. It is generally given in  $\text{g/m}^2$ . It may be determined by weighing a phosphatised metal sheet having a known surface area, dissolving the metal phosphate layer and weighing the metal sheet again. The weight of metal phosphate layer with reference to one  $\text{m}^2$  may be calculated from the weight difference determined, by taking account of the surface area of the metal sheet. A 0.5 wt. % strength chromic acid solution, for example, may be used to dissolve

30 the metal phosphate layer. The procedure for determining the weight per unit area is described in more detail in German standard DIN 50942.

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The weight per unit area is an essential parameter for checking phosphatising results. Weights per unit area within a variety of ranges may be required, depending on the intended use for the phosphatised metal parts. The present invention is preferentially concerned with metal  
5 sheeting which is to be used in the car manufacturing industry. In this case, weights per unit area of more than  $0.8 \text{ g/m}^2$ , but at most about  $4 \text{ g/m}^2$ , are required. The weight per unit area should preferably be below  $3 \text{ g/m}^2$  and in particular about 1 to about  $2 \text{ g/m}^2$ .

Each of the components (a), (b) and (c) boosts the effect of the others as an inhibitor of the  
10 pickling reaction at the non-galvanised steel face. Thus, phosphatising of the non-galvanised steel face is inhibited more effectively and more reliably if the phosphatising solution contains at least two of components (a), (b) and (c). The phosphatising solution preferably contains all three components (a), (b) and (c).

15 Component (a) may be selected, for example, from the acetylenically unsaturated diols. A preferred example such is but-2-yne-1,4-diol.

Alkyl or alkenyl amines, for example, are suitable for use as component (b). Furthermore, alkyl- or alkenyl-substituted nitrogen-containing heterocyclic compounds, in particular  
20 unsaturated heterocyclic compounds are especially suitable. These may have, for example, 1, 2 or 3 nitrogen atoms in the heterocyclic ring. One alkyl group is preferably in a position which is located as far as possible from the nitrogen atom(s). Particularly preferred examples are mono- and di-alkylpyridines having 1 to 22, preferably 1 to 12, carbon atoms in each alkyl group, wherein one alkyl group is preferably in the 4-position with respect to the  
25 nitrogen atom. These alkylated pyridines are generally available as a technical grade mixture.

Due to the fact that it is industrially readily available, potassium iodide is preferably used as component (c).

30 In addition to components (a), (b) and/or (c), the phosphatising solution may contain up to  $250 \text{ mg/l}$ , preferably about 40 to  $80 \text{ mg/l}$ , of a non-ionic surfactant. In combination with at



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least one of components (a), (b) and/or (c), this surfactant supports the inhibiting effect on the non-galvanised steel face. Ethoxylated, propoxylated and/or ethoxylated/propoxylated alcohols having 10 to 18 carbon atoms in the alkyl chain are preferably used as non-ionic surfactants. In addition to the non-ionic surfactant, the phosphatising solution may contain a  
5 solubility promoter for the surfactant. This may be present at a concentration of up to 750 mg/l, preferably about 150 to about 300 mg/l. Cumene sulfonate, for example, is suitable for use as a solubility promoter.

Apart from the components (a), (b) and/or (c) required for the inhibiting effect on the non-  
10 galvanised steel face, the phosphatising solution may contain other components commonly used in the prior art which either become incorporated into the phosphate layer or, due to the accelerator effect thereof, promote formation of the layer. Accordingly, the phosphatising solution preferably also contains one or more of the following cations:

- 1 to 5 g/l of manganese ions,
- 15 1 to 4 g/l of magnesium ions,
- 0.8 to 4.5 g/l of nickel ions,
- 0.01 to 0.2 g/l of copper ions.

In addition to the layer-forming cations mentioned, the phosphatising solutions contain alkali  
20 metal and/or ammonium cations in order to adjust the free acid value to within the required range.

Conventionally, phosphatising baths also contain so-called accelerators. These are substances which react with the hydrogen being produced during the pickling reaction at the metal  
25 surface. They therefore inhibit so-called polarisation of the metal surface caused by a coating of hydrogen. The accelerators thus improve uniform coating of the metal surface with finely divided phosphate crystals, which generally have a size between about 1 and about 10  $\mu$ m. Phosphatising solutions which contain the accelerator are also preferably used in the process according to the present invention. Accordingly, the phosphatising solutions used for the  
30 present process also contain, as accelerator, one or more of the following components:

- 0.5 to 30 g/l of nitrate ions,

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0.05 to 0.2 g/l of nitrite ions,

0.03 to 0.2 g/l of hydrogen peroxide in the free or bound form,

0.05 to 0.6 g/l of permanganate ions.

- 5 Alternatively, or in the event that nitrate ions are used, in addition to these, a phosphatising solution which also contains, as accelerator, about 0.1 to about 3 g/l of hydroxylamine in the free, ionic or bound form is preferably used for the process according to the present invention.
- 10 Hydroxylamine may be used as the free base, as a compound which releases hydroxylamine, such as hydroxylamine complexes or ketoximes or aldoximes, or in the form of hydroxylammonium salts. If free hydroxylamine is added to the phosphatising bath or a phosphatising bath concentrate, then this is largely present as the hydroxylammonium cation due to the acidic character of these solutions. If it is used in the form of a hydroxylammonium
- 15 salt, then sulfates and phosphates are particularly suitable. In the case of phosphates, acid salts are preferred due to the higher solubility thereof. In order, on the one hand, to take account of economic aspects and, on the other hand, not to contaminate the phosphatising baths too much with sulfate ions, it may be advantageous to use a combination of free hydroxylamine and hydroxylammonium sulfate. Hydroxylamine or compounds thereof are
- 20 added to the phosphatising solution in an amount such that the calculated concentration of free hydroxylamine is between about 0.1 and about 3 g/l, preferably between about 0.15 and about 1 g/l.

When quoting data relating to the concentration of phosphate, the entire amount of

25 phosphorus in the phosphatising bath is regarded as being present in the form of phosphate ions,  $\text{PO}_4^{3-}$ . Therefore, when calculating or determining the concentration, the known fact that, at the acidic pHs prevailing in phosphatising baths, in the range from about 2.0 to about 3.6, only a very small proportion of the phosphate is actually in the form of triply charged anions, is ignored. Rather, it would be expected, at these pHs, that the phosphate is probably

30 present as a singly charged dihydrogen phosphate anion, together with undissociated phosphoric acid and small amounts of doubly charged hydrogen phosphate anions.

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The presence of fluoride ions may be advantageous for uniform production of the layer. Accordingly, there is a further embodiment of the present invention comprising using phosphatising solutions which contain up to about 0.8 g/l of fluoride in the free or complexed  
5 form. The preferred fluoride concentrations for phosphatising electrolytically galvanised steel strip, for example, is in the range from 0.0 to about 0.5 g/l, in particular in the range from about 0.1 to about 0.2 g/l.

The phosphatising solutions are generally prepared in the way which is familiar to a person  
10 skilled in the art. Phosphate is introduced to the phosphatising solutions, for example, in the form of phosphoric acid. The cations are added to the phosphoric acid in the form of acid-soluble compounds, such as carbonates, oxides or hydroxides, so that the acid is partly neutralised. Further neutralisation to reach the desired pH range is preferably performed by adding sodium hydroxide or sodium carbonate. Sodium or potassium fluoride, for example,  
15 are suitable as sources of free fluoride anions. Tetrafluoroborate or hexafluorosilicate, for example, may be used as complex fluorides.

In order to produce phosphate layers having a weight per unit area in the desired range, phosphatising solutions which have a concentration of free acid in the range from about 0.4 to  
20 about 4 points and a concentration of total acid in the range from about 15 to about 45 points are preferably used. The expressions "free acid" and "total acid" and methods for determining them are explained below. The values for free acid are preferably between about 1.5 and about 3.5 and in particular between about 2.0 and about 3.0 points. The concentration of total acid is preferably in the range from about 25 to about 35 points.

25 The expressions "free acid" and "total acid" are generally known in the phosphatising field. They are determined by titrating the acid bath sample with 0.1 normal caustic soda solution and determining how much is consumed. The amount consumed in ml is quoted as the numerical points value. Herein, the points value for free acid is the number of ml of 0.1N  
30 caustic soda solution consumed in order to achieve pH 4.0 in 10 ml of bath solution which has been diluted to 50 ml using fully deionised water. In the same way, the points value for total

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acid is the number of ml consumed in order to achieve pH 8.2.

The temperature of the phosphatising solution in the present process is preferably in the range from about 50 to about 70°C and in particular is between 53 and 65°C.

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In the process according to the present invention, the steel strip which has been galvanised on one face is contacted with the phosphatising solution for a period in the range from about 2 to about 30 seconds by spraying the phosphatising solution onto the galvanised steel strip or by immersing the galvanised steel strip in the phosphatising solution. Spray treatment is a simpler procedure and is thus preferred. Treatment times between 3 and 15 seconds are particularly preferred. After the desired treatment time, the phosphatising solution is rinsed off the galvanised steel strip using water.

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The process according to the present invention is preferably adjusted so that crystalline zinc phosphate layers having weights per unit area in the range 1 to 2 g/m<sup>2</sup> are produced on the galvanised face of the steel strip which has been galvanised on one face.

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Before applying the phosphatising solution, the metal surface must be fully water-wettable. This is generally the case with a continuously operating conveyer belt system. However, if the surface of the strip has been oiled, this oil must be removed using an appropriate cleanser prior to phosphatising. Processes for this are known in the industry. Activation using activating agents known from the prior art is generally performed before phosphatising. Solutions or suspensions which contain titanium phosphate and sodium phosphate are generally used. Use of the present phosphatising process follows activation, and phosphatising may advantageously be followed by a passivating post-rinsing procedure. Intermediate water rinsing is generally performed between the phosphatising and passivating post-rinsing procedures. Chromic acid-containing treatment baths are widely used for passivating post-rinsing. However, for reasons of occupational health and safety and in order to protect the environment, and also for waste disposal reasons, there is the tendency to replace these chromium-containing passivating baths with chromium-free treatment baths. Purely inorganic bath solutions, in particular those based on hexafluorozirconates, or organic-reactive bath

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solutions, for example those based on substituted poly(vinylphenols), have been disclosed for this purpose. Furthermore, post-rinsing solutions which contain 0.001 to 10 g/l of one or more of the following cations may be used: lithium ions, copper ions, silver ions and/or bismuth ions.

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Metal strip which has been phosphatised according to the present invention may be directly provided with an organic surface coating. However, they may also be assembled, in the initially unlacquered state, to make structural components such as car body parts or domestic appliances, by cutting, shaping and joining together. The forming processes associated with this procedure are facilitated by the phosphate layer. If exposure of the final structural component to corrosive effects is low, for example as in the case of domestic appliances, the appliances assembled from pre-phosphatised metal may be directly lacquered. If exposure to corrosive effects is more severe, as is the case, for example, in the car industry, it may be advantageous to follow assembly of the body with another phosphatising treatment. When performing this subsequent phosphatising treatment, or during the cleansing procedure preceding this, inhibiting compounds (a), (b) and/or (c) must be sufficiently well removed from the non-galvanised steel face for the subsequent phosphatising process not to be impaired.

20 The present invention also relates to use of an aqueous solution which contains water and, with reference to the total composition,

- (a) 10 to 30 wt. % of one or more mono- or poly-hydric alcohols having at least one carbon-carbon triple bond,
- (b) 1.6 to 4.8 wt. % of one or more alkyl or alkenyl nitrogen compounds having at least 5 carbon atoms, and
- (c) 2.4 to 7.2 wt. % of alkali metal iodide, as an additive to a phosphatising solution for phosphatising the galvanised face of steel which has been galvanised on one face.

Preferred examples of components (a) (b) and (c) are given above.

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The aqueous solution for use according to the present invention preferably also contains 2 to 8

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wt. % of one or more non-ionic surfactants, which have also been characterised in more detail above. The surfactant additive improves the intended object of the present invention, that is to protect from phosphatising the non-galvanised steel face on steel strip which has been galvanised on one face. An aqueous solution which contains, in addition to the non-ionic  
5 surfactant, a solubility promoter for this surfactant is preferably used for this purpose. Cumene sulfonate, for example, is suitable here. Sufficient solubility promoter is used to produce a clear surfactant solution.

The use according to the present invention proceeds in such a way that the aqueous solution  
10 of components (a), (b) and (c) is added in an amount between 0.15 and 1 vol. % of the phosphatising solution. The amount added is selected so that the phosphatising solution contains components (a), (b) and (c) in the following concentration ranges:

- (a) 60 to 1000 mg/l of one or more mono- or poly-hydric alcohols having at least one carbon-carbon triple bond,
- 15 (b) 10 to 160 mg/l of one or more alkyl or alkenyl nitrogen compounds having at least 5 carbon atoms, and
- (c) 10 to 250 mg/l of an alkali metal iodide.

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Examples

The process according to the present invention was tested in a laboratory phosphatising unit. Sample sheets which had been electrolytically galvanised on one face were activated using a titanium phosphate-containing activating solution (Fixodine® 950, Henkel KGaA, batch concentration; 0.5 wt.%) and phosphatised under the conditions given in the Table. In addition to the values given in the Table, the phosphatising bath had the following composition:

- 10 3.5 g/l of zinc,
- 3.0 g/l of manganese,
- 3.0 g/l of nickel,
- 17 g/l of phosphate ions,
- 15 g/l of nitrate ions,
- 15 Free acid, 2 - 2.5 points
- Total acid, 30 - 35 points
- Temperature, 58°C
- Treatment time, 10 seconds (spraying).

- 20 These values correspond to the commercially used phosphatising process GRANODINE® 5854 (Henkel Surface Technologies).

The Table contains the following observations relating to the efficiency of the phosphatising process according to the present invention:

- 25 I. The extent of crystal formation on the non-galvanised face
- II. The concentration of divalent iron ions in the phosphatising solution after phosphatising an area of 5 m<sup>2</sup> per l of phosphatising solution. The lower the concentration of divalent iron ions accumulating in the bath, the more effective is inhibition of the pickling reaction on the non-galvanised face.
- 30 III. The weight per unit area in g/m<sup>2</sup> on the non-galvanised steel face during subsequent phosphatising using a phosphatising bath corresponding to the prior art for

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phosphatising car bodies (GRANODINE® SP 2500, Henkel Surface Technologies). This subsequent phosphatising process was performed at a temperature of 55°C for a period of 120 seconds.

- 5 During this test of the phosphatising process according to the present invention, independently of adding components (a), (b) and (c), a sealed layer of zinc phosphate crystals having a size in the range from 3 to 5µm and a weight per unit area of 1.3 to 1.4 g/m<sup>2</sup> was obtained. Phosphatising the galvanised face is thus not affected by adding the components acting as inhibitors for the steel face.



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Table: Phosphatising bath additives (in mg/l) and phosphatising results

Example no.	a) but-2-yne-1,4-diol	b) Mixture of C <sub>1</sub> -C <sub>10</sub> mono- and di-alkylated pyridines	c) potassium iodide	l) Appearance of steel face	mg of Fe(II) after use	Weight per unit area (steel face) after second phosphatising
Comp. 1	0	0	0	heavy crystal formation	60 mg/l	<1.0
Ex. 1	60	9.6	14.4	crystal nests	40 mg/l	<1.0
Ex. 2	140	22.4	33.6	isolated crystal nests	30 mg/l	≤ 1.2
Ex. 3	200	32.0	48.0	shiny	<8 mg/l	≥1.8
Ex. 4	300	48.0	72.0	shiny	<8 mg/l	≥1.8
Ex. 5	600	96.0	144.0	shiny	<8 mg/l	≥1.8
Ex. 6	1000	160	240	shiny	<8 mg/l	1.8 - 2.4

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Claims:

1. A process for phosphatising the galvanised face of steel strip which has been galvanised on one face using a phosphatising solution which contains 1 to 6 g/l of zinc ions and 10 to 30 g/l of phosphate ions, characterised in that the phosphatising solution also contains one or more of the components (a) to (c):
  - (a) 60 to 1000 mg/l of one or more mono- or poly-hydric alcohols having at least one carbon-carbon triple bond,
  - (b) 10 to 160 mg/l of one or more alkyl or alkenyl nitrogen compounds having at least 5 carbon atoms,
  - (c) 10 to 250 mg/l of an alkali metal iodide.
2. A process as claimed in claim 1 wherein the phosphatising solution contains one or more of components (a) to (c):
  - (a) 200 to 400 mg/l of one or more mono- or poly-hydric alcohols having at least one carbon-carbon triple bond,
  - (b) 30 to 60 mg/l of one or more alkyl or alkenyl nitrogen compounds having at least 5 carbon atoms,
  - (c) 40 to 100 mg/l of an alkali metal iodide.
3. A process as claimed in one or both of claims 1 and 2 wherein the phosphatising solution contains at least two of components (a), (b) and (c).
4. A process as claimed in claim 3 wherein the phosphatising solution contains all three components (a), (b) and (c).
5. A process as claimed in one or more of claims 1 to 4 wherein the phosphatising solution also contains one or more of the following cations:
  - 1 to 5 g/l of manganese ions,
  - 1 to 4 g/l of magnesium ions,

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0.8 to 4.5 g/l of nickel ions,  
0.01 to 0.2 g/l of copper ions.

- 5 6. A process as claimed in one or more of claims 1 to 5 wherein the phosphatising solution also contains one or more of the following components as an accelerator:  
0.5 to 30 g/l of nitrate ions,  
0.05 to 0.2 g/l of nitrite ions,  
0.03 to 0.2 g/l of hydrogen peroxide in the free or bound form,  
10 0.05 to 0.6 g/l of permanganate ions.
7. A process as claimed in one or more of claims 1 to 5 wherein the phosphatising solution also contains 0.1 to 3 g/l of hydroxylamine, in free, ionic or bound form, as an accelerator.
- 15 8. A process as claimed in one or more of claims 1 to 7 wherein the phosphatising solution has a concentration of free acid in the range 0.4 to 4 points and a concentration of total acid in the range 15 to 45 points.
- 20 9. A process as claimed in one or more of claims 1 to 8 wherein the phosphatising solution has a temperature in the range 50 to 70°C.
10. A process as claimed in one or more of claims 1 to 9 wherein the phosphatising solution is contacted, by spraying or by immersion, with the steel strip which has been galvanised on one face for a period of 2 to 30 seconds.
- 25 11. A process as claimed in one or more of claims 1 to 10 wherein the phosphate layer on the galvanised face of the steel strip which has been galvanised on one face is produced having a weight per unit area in the range 1 to 2 g/m<sup>2</sup>.
- 30 12. The use of an aqueous solution which contains water and, with reference to the total composition,

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- (a) 10 to 30 wt.% of one or more mono- or poly-hydric alcohols having at least one carbon-carbon triple bond,
- (b) 1.6 to 4.8 wt.% of one or more alkyl or alkenyl nitrogen compounds having at least 5 carbon atoms, and
- 5 (c) 2.4 to 7.2 wt.% of an alkali metal iodide, as an additive to a phosphatising solution for phosphatising the galvanised face of steel which has been galvanised on one face and which contains 1 to 6 g/l of zinc ions and 10 to 30 g/l of phosphate ions.
- 10 13. A use as claimed in claim 12 wherein the aqueous solution also contains 2 to 8 wt.% of one or more non-ionic surfactants.
14. A use as claimed in one or both of claims 12 and 13 wherein the aqueous solution is added to the phosphatising solution in an amount between 0.15 and 1 vol. %.